

Report No. 03-68-89

First Quarterly Report

SOLAR CELL CONTACT DEPOSITION PARAMETER STUDY

(30 August 1968—30 November 1968)

Contract No. NAS5-11612
Goddard Space Flight Center
Contracting Officer: J. A. Maloney
Technical Monitor: John W. Fairbanks

Prepared by

Texas Instruments Incorporated
Components Group
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Project Engineer: Gayle Morrison

for

Goddard Space Flight Center
Greenbelt, Maryland 20771

FACILITY FORM 602	N71-74308	
	(ACCESSION NUMBER)	(THRU)
	37	None
	(PAGES)	(CODE)
OK-119269		(CATEGORY)
(NASA CR OR TMX OR AD NUMBER)		



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SUMMARY

The object of this report is to present the progress for the first three-month period of a six-month study program to improve vacuum deposition parameters of titanium-silver contacts deposited on silicon solar cells.

The scope of this study program (phase 2 of a 3-phase program—Ref: NASA RFP 716-90066/285) is to identify the relationship between various contact evaporation parameters and the humidity resistance of the solar cell Ti-Ag contact. Work this period has evaluated the effects of various evaporation substrate temperatures from 0°C to 200°C. Evidence is presented, in the form of electron microscope photos, which shows that the grain size of the evaporated silver contact becomes larger when the evaporation substrate temperature is increased. This effect was expected since it has been established that the grain size of an evaporated metal film depends, to a great extent, on the mobility of the evaporated surface atoms, and this mobility is influenced by an increase or decrease in substrate temperatures. Data are presented which indicate that solar cell Ti-Ag contacts having the smallest grain size do exhibit a higher degree of humidity resistance. It is felt, however, that this effect is not the complete answer for a long-term high-reliability solar cell contact.

TABLE OF CONTENTS

SECTION	TITLE	PAGE
I.	INTRODUCTION	1
	A. Objective	1
	B. Scope of Work	1
II.	TECHNICAL DISCUSSION	3
	A. Sample Fabrication and Test	3
	1. Material	3
	2. Equipment & Methods	3
	a. Evaporation	3
	b. Electrical Test	3
	c. Environmental	4
	d. Electron Microscopy	4
	e. Film Thickness	4
	B. Experimental Results	4
	1. Substrate Temperatures	4
	a. 200°C Substrate Temperature	4
	b. 150°C Substrate Temperature	6
	c. 100°C Substrate Temperature	6
	d. 50°C Substrate Temperature	13
	e. 0°C Substrate Temperature	13
	2. Sintering Gases	14
	3. Contact Silver Thickness	14
III.	NEW TECHNOLOGY	21
IV.	PROGRAM FOR NEXT REPORTING PERIOD	23
V.	CONCLUSIONS AND RECOMMENDATIONS	25

LIST OF ILLUSTRATIONS

FIGURE	TITLE	PAGE
1.	Process Flow Diagram	5
2.	200°C Contacts After Environmental Testing	7
3.	200°C Contacts Electron Microscope Photos	8
4.	150°C Contacts After Environmental Testing	9
5.	150°C Contacts Electron Microscope Photos	10
6.	100°C Contacts After Environmental Testing	11
7.	100°C Contacts Electron Microscope Photos	12
8.	50°C Contacts Electron Microscope Photos	16
9.	50°C Contacts After Environmental Testing	17
10.	0°C Contacts Electron Microscope Photos	18
11.	Contacts Sintered in Different Ambient Gases	19

LIST OF TABLES

TABLE	TITLE	PAGE
I.	200°C Substrate Electrical Data	6
II.	150°C Substrate Electrical Data	13
III.	100°C Substrate Electrical Data	14
IV.	50°C Substrate Electrical Data	15
V.	0°C Substrate Electrical Data	15

SECTION I

INTRODUCTION

A. OBJECTIVE

One of the biggest problems currently encountered with silicon solar cells is the power degradation attributable to the Ti-Ag contacts. The objective of this study program is to determine the extent of contribution of the various parameters involved with the Ti-Ag contact deposition.

B. SCOPE OF WORK

The program has involved the fabrication of a large number of experimental lots of silicon solar cells. Cells have been fabricated on which the contact evaporation substrate temperature was maintained at 200°C, 150°C, 100°C, 50°C, and 0°C. Data are presented on these cells both before and after an accelerated life test consisting of storage for ten (10) days at a relative humidity of 95 percent and an ambient temperature of 45°C. Cells have also been fabricated on which the thickness of the contact silver is 3, 5, 7, and 10 microns. These cells are in the accelerated life test chamber at the time of this writing. Presented in this report are data on a group of cells, fabricated with TI funding, on which the ambient sintering gases were varied. The gases used were nitrogen, helium, hydrogen, and forming gas (10% H + 90% N).

SECTION II

TECHNICAL DISCUSSION

A. SAMPLE FABRICATION AND TEST

Every possible measure was taken to ensure that all samples were processed identically, except for the parameters varied for evaluation. Presented below is a brief discussion of the material, equipment, and methods used.

1. Material

Silicon blanks used were of the standard P-type 2 cm × 2 cm × 13 mil size with a base resistivity of 7 to 14 ohm-cm. The N-type phosphorous-diffused layer is approximately 3500 Å in depth. Titanium and silver charges used in the contact evaporation are specified as being 99.99 percent pure.

2. Equipment & Methods

a. Evaporation

Titanium-silver contacts were deposited using a Model 18 Consolidated Vacuum Corporation vacuum system. Titanium charges were evaporated using tungsten coils and the silver charges were evaporated from tantalum boats. All evaporations were made in the upward direction, with the substrates facing downward from the top of the bell jar. For substrate temperatures from 50°C to 200°C, an infrared heating system was mounted directly to the substrate holders. For the evaporation made with a substrate temperature of 0°C, liquid nitrogen was circulated through copper coils which were attached directly to the substrate holders. Substrate temperatures were monitored with a West Model IN-3 potentiometer using an iron-constantan thermocouple located between the substrate holders and the substrates.

b. Electrical Test

Electrical output tests. These electrical data are presented in the Experimental Results portion of this section and indicate the effect of each experiment on the degradation resistance of the sample solar indicates the effect of each experiment on the degradation resistance of the sample solar cell's contacts. For these electrical output tests, a tungsten light source was used consisting of three tungsten flood lamps operated at a color temperature of $2800^{\circ}\text{K} \pm 50^{\circ}\text{K}$ and adjusted to the height necessary to attain air-mass-zero intensity. The light source intensity was calibrated using an in-house AMO working standard, which was calibrated with JPL balloon standard No. 185. The tungsten light source was chosen over TI solar simulator for expediency and accuracy on the comparative nature of the testing.

c. Environmental

Accelerated storage life testing, consisting of ten days' storage at a temperature of 45°C and a relative humidity of 95 percent, was performed on samples from each experiment. Samples were stored in a Blue M model No. CF-7216A humidity chamber.

d. Electron Microscopy

Photos of the grain structure and size of the deposited silver contacts were made using a TI R.C.A. EMU 3 electron microscope.

e. Film Thickness

Titanium-silver contact thicknesses were monitored with a Taylor Hobson Model 3 Talysurf instrument.

B. EXPERIMENTAL RESULTS

1. Substrate Temperatures

For this experiment, solar cells were fabricated as per the normal TI process outlined in Figure 1. Contact evaporation substrate temperatures were closely monitored to assure close tolerance (+10°C/−5°C) to the different temperatures reported. Sample cells from each evaporation were subjected to a tape test, prior to environmental testing, to assure good contact integrity at the start of testing. Contacts for this experiment were nominally 5-microns thick. Evaluation groups reported on are:

Group D—200°C Substrate Temperature

Group C—150°C Substrate Temperature

Group B—100°C Substrate Temperature

Group A— 50°C Substrate Temperature

Group E— 0°C Substrate Temperature

It should be noted at this point that the sintering process (600°C) following contact deposition, will affect the contact grain size and structure. Data presented here are on cells which have been sintered, but for comparative evaluations these data are considered valid.

a. 200°C Substrate Temperature—Group D

Table I gives the compiled electrical data, before and after environmental testing, from the 200°C substrate contact evaporation experiment. Five cells in this group exhibited an electrical degradation greater than 4.5 percent at the maximum power point, while two of those five cells almost entirely lost their electrical output. All cells in this group exhibited contact delaminations, blisters, peeling, cracking, etc., as shown in Figure 2 after environmental testing. Electron microscope analyses of these contacts, before environmental exposure, revealed large silver grain boundaries with visible cracks in the grain boundary area, as shown in Figure 3.

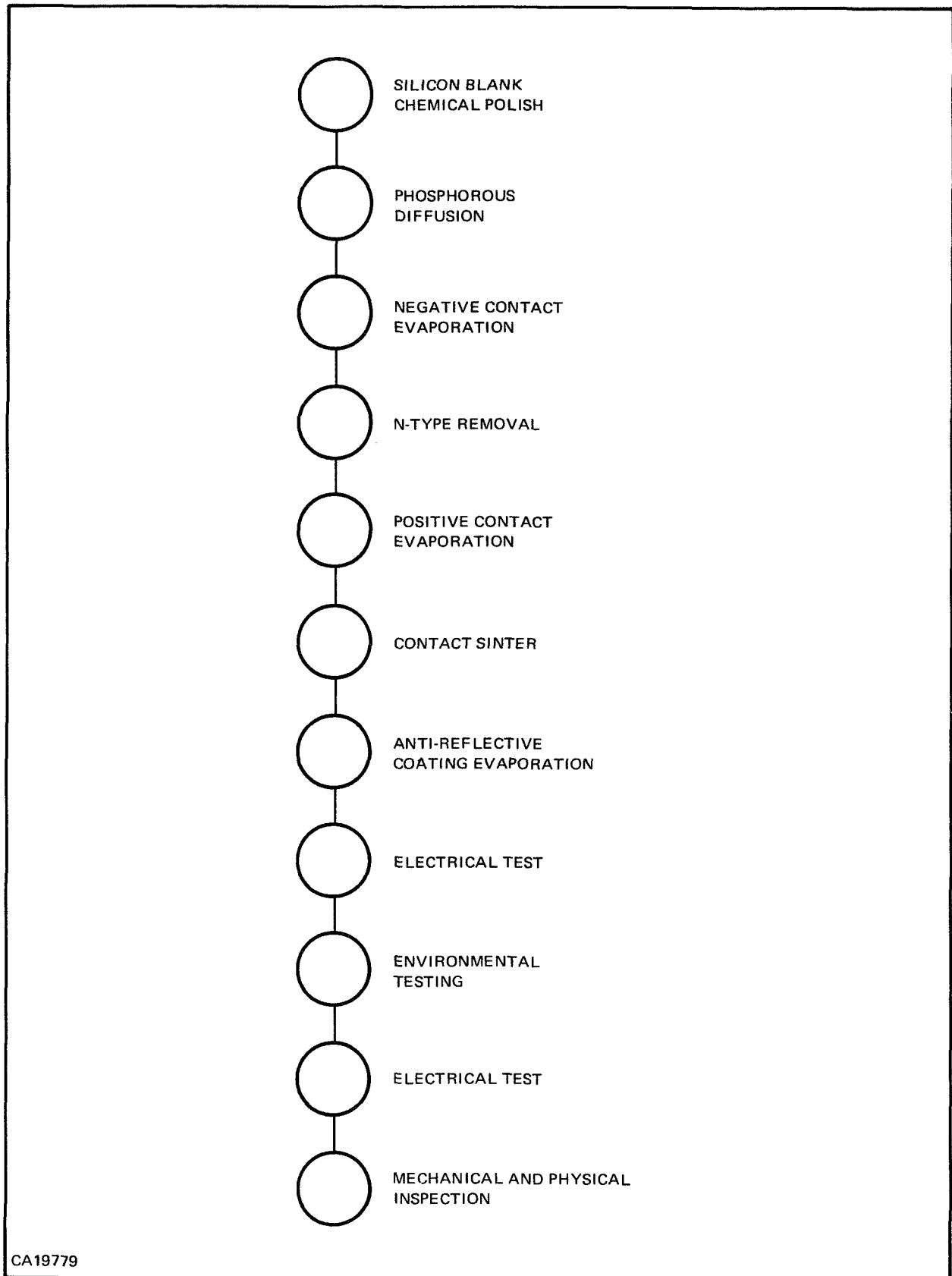


Figure 1. Process Flow Diagram

Table I. 200°C Substrate Electrical Data

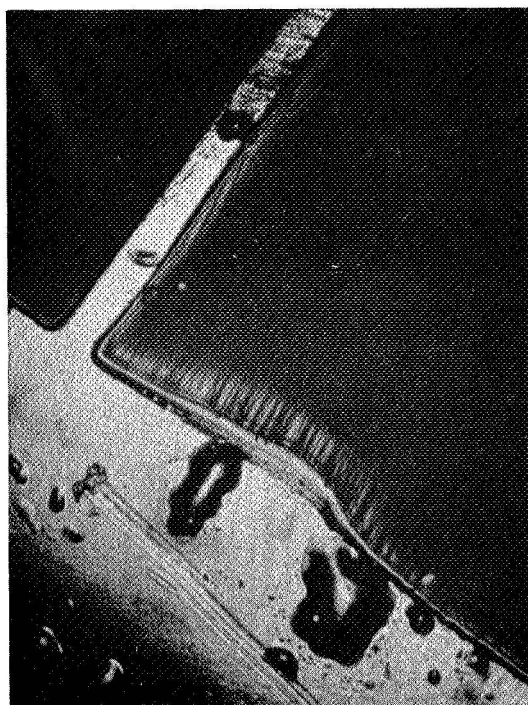
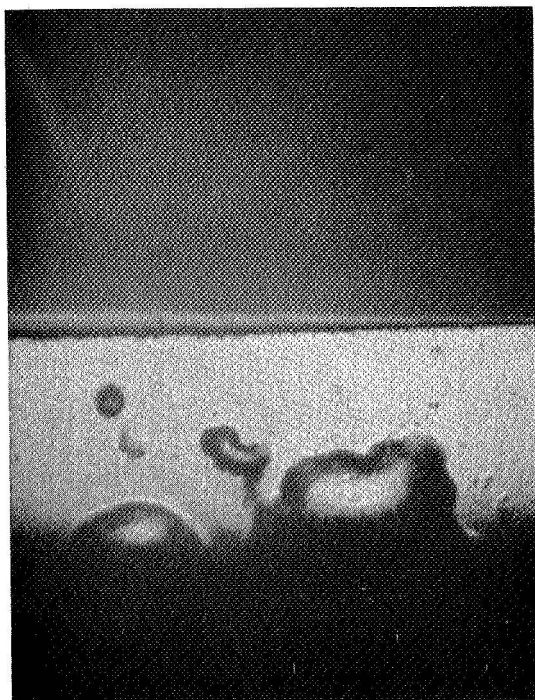
Cell No.	I_{SC} (mA)	I_{SC} (mA)	Δ	V_{OC} (mV)	V_{OC} (mV)	Δ	I at 430 mV (mA)	I at 430 mV (mA)	Δ
	Initial	Post	(mA)	Initial	Post	(mV)	Initial	Post	(mA)
Control Cell	150.0	150.5	0	543	543	0	138	138.2	0
D-1	146.0	137.3	-8.7	562	545	-17	138	6.0	-132
D-2	147.0	21.0	-126	558	545	-13	139	4.0	-135
D-3	143.0	146.5	+3.5	560	560	0	136	120.0	-16
D-4	147.0	148.0	+1	560	555	-5	138	120.0	-18
D-5	146.0	146.0	0	558	550	-8	138	137.5	-0.5
D-6	148.5	148.5	0	555	554	-1	141	134.0	-7
D-7	148.0	148.5	+0.5	550	550	0	139	136.0	-3
D-8	148.0	148.0	0	557	557	0	138	138.0	0
D-9	148.0	148.0	0	560	560	0	141	141.0	0
D-10	147.0	147.0	0	553	553	0	137	137.0	0
Average	146.8	133.9	-12.9	557.3	552.9	-4.4	138.5	107.4	-31.1

b. 150°C Substrate Temperature—Group C

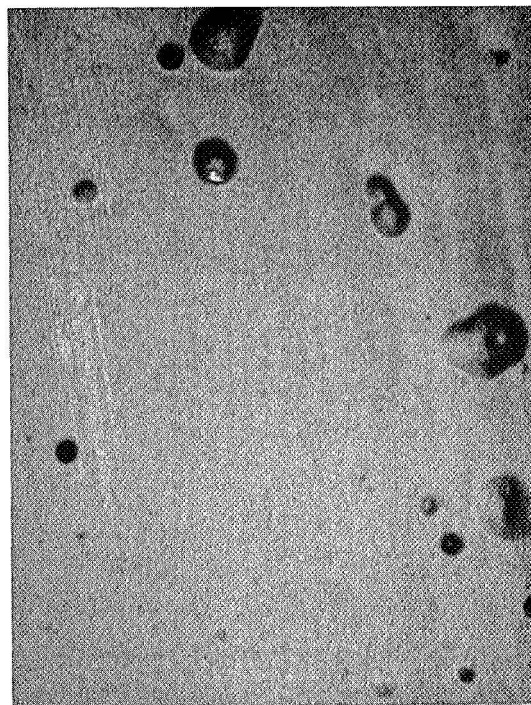
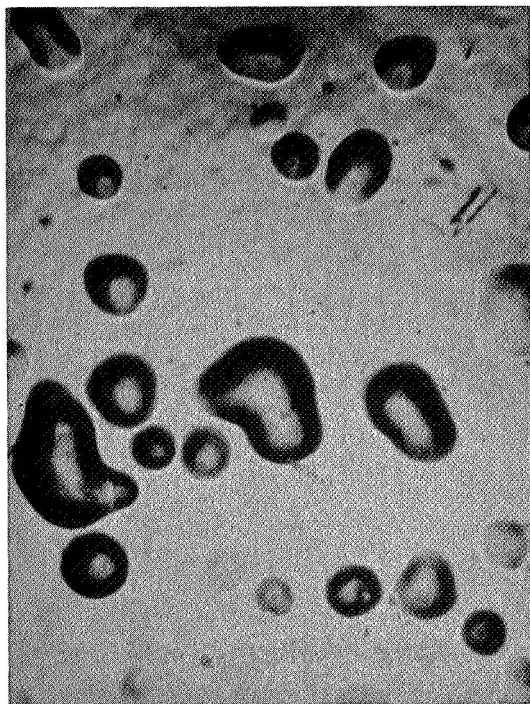
Table II gives the compiled electrical data, before and after environmental testing, from the 150°C substrate contact evaporation experiment. Three cells in this group exhibited an electrical degradation greater than 4.5 percent at the maximum power point. Following environmental exposure, all cells in this group had contact delaminations occurring similar to those in Group D (see Figure 2). Four cells in this group exhibited even more severe blistering on the "P" contact as shown in Figure 4. The electron microscope analysis of this group revealed a silver contact grain structure very similar to that found on the Group D cells. The electron microscope photos of this group are shown in Figure 5.

c. 100°C Substrate Temperature—Group B

Two cells from this group had electrical output losses greater than 4.5 percent with one cell suffering a 98 percent drop in output at 430 millivolts. Table III shows the electrical results from this experiment. Physical contact delaminations were almost identical to those experienced by Group C with the exception of the grids and N-contact collector which did not have blistering and peeling as serious as those of Groups C or D. It is felt that the intact grids of this group maintained a low series resistance for electron movement on the active surface of the cells and thus resulted in a more favorable post-test electrical output. The "P" contacts of this group (see Figure 6) would not survive solar panel interconnection processes following environmental testing. The entire "P" contact of cell No. B-8 separated from the silicon causing the electrical output losses shown in Table III. Electron microscope photos (see Figure 7) of this group revealed a slightly smaller grain size but the cracks in the grain boundary areas were still in evidence.



200°C N-CONTACT BLISTERS (60X)



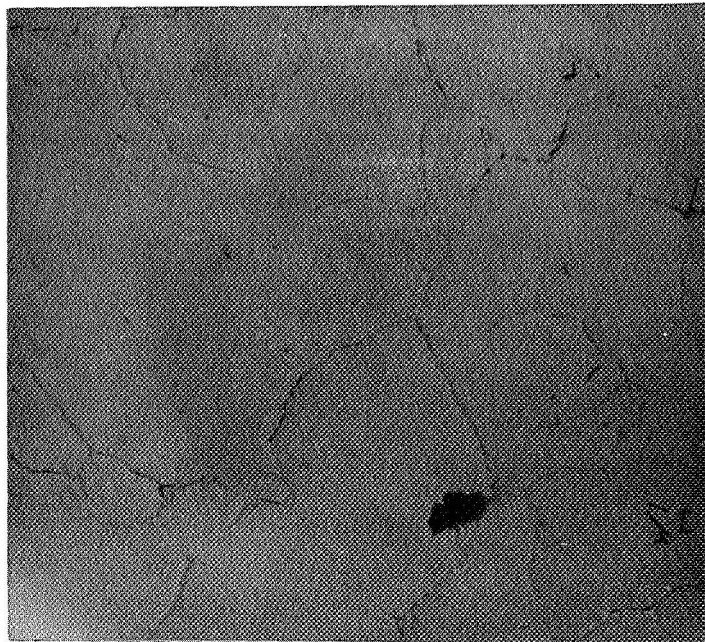
CA19780

200°C P-CONTACT BLISTERS (60X)

Figure 2. 200°C Contacts After Environmental Testing



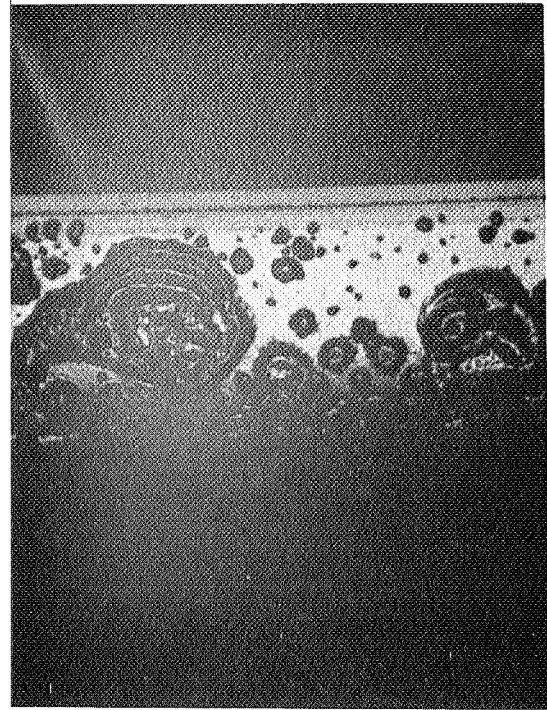
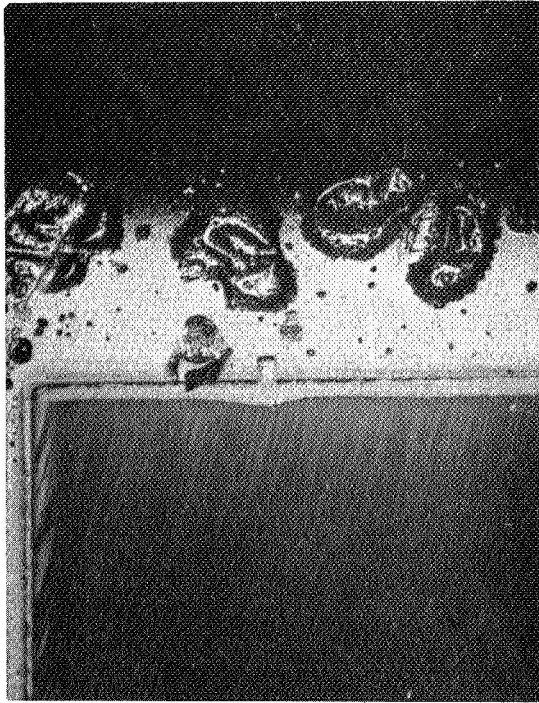
200°C CONTACT ELECTRON MICROSCOPE
PHOTO POSITIVE REPLICA



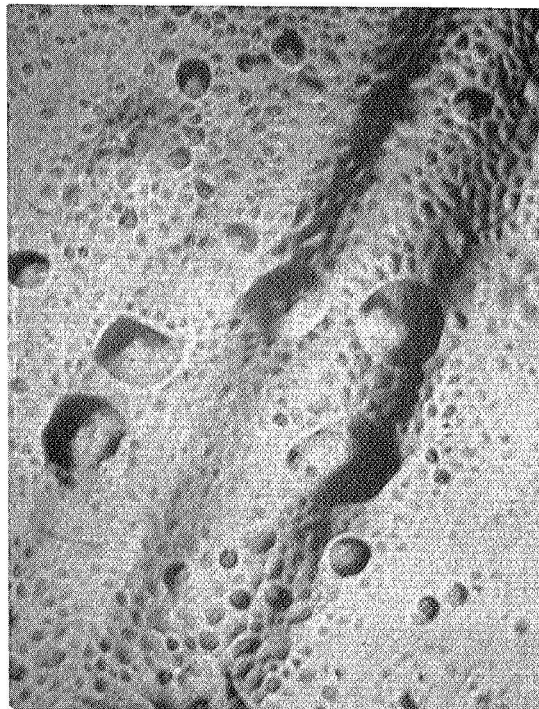
200°C CONTACT ELECTRON MICROSCOPE
PHOTO NEGATIVE REPLICA

CA19781

Figure 3. 200°C Contacts Electron Microscope Photos



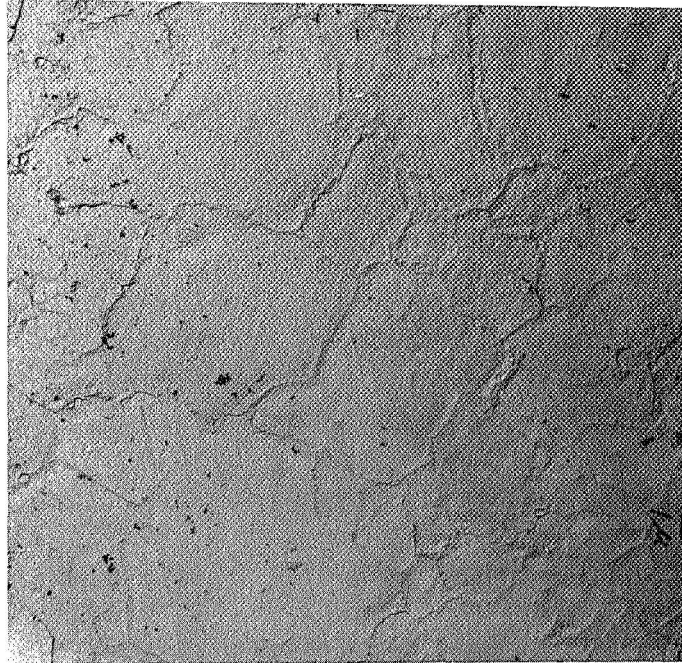
150°C N-CONTACT BLISTERS (60X)



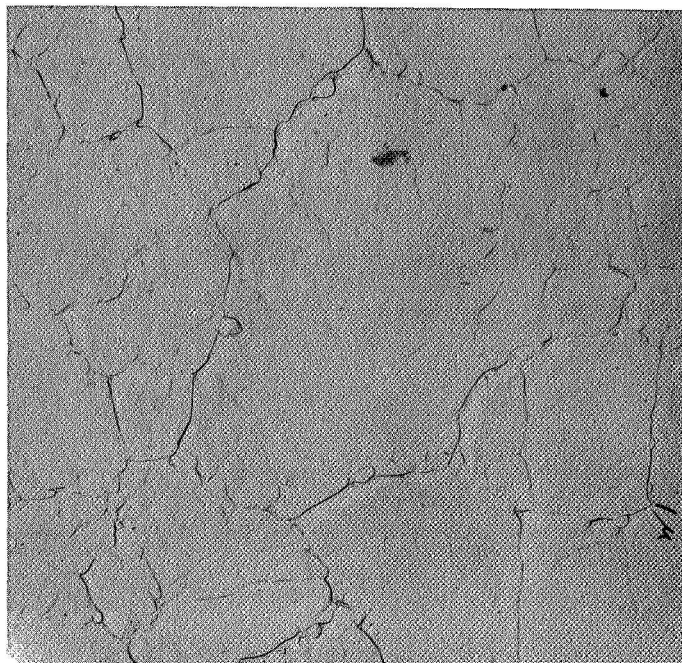
150°C P-CONTACT BLISTERS (60X)

CA19782

Figure 4. 150°C Contacts After Environmental Testing



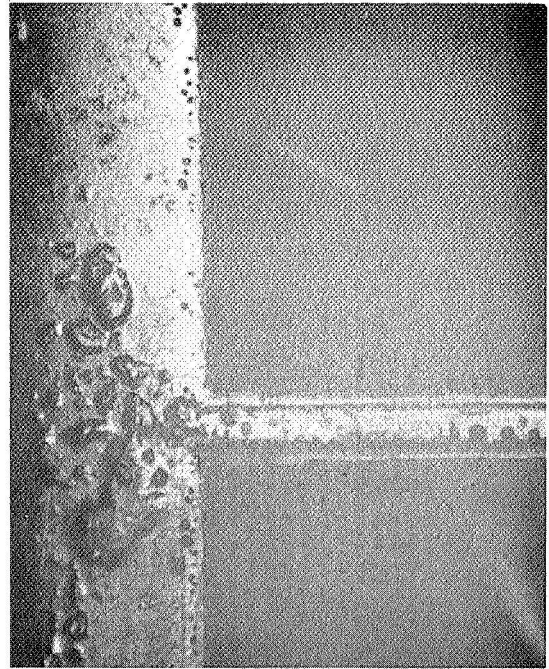
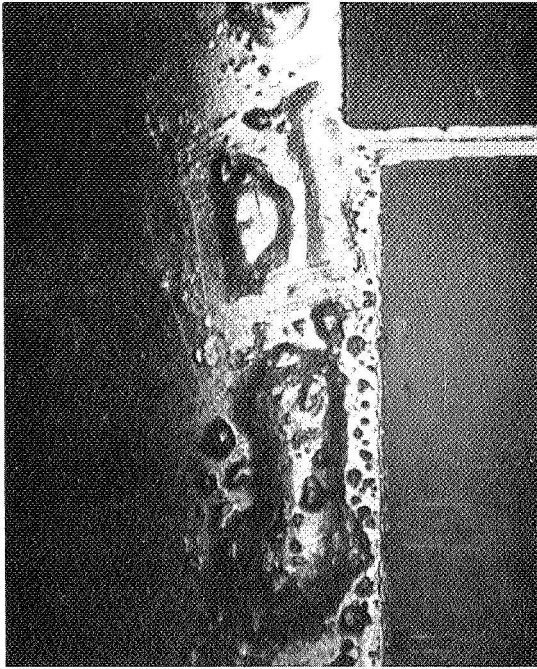
150°C CONTACT ELECTRON MICROSCOPE
PHOTO POSITIVE REPLICA



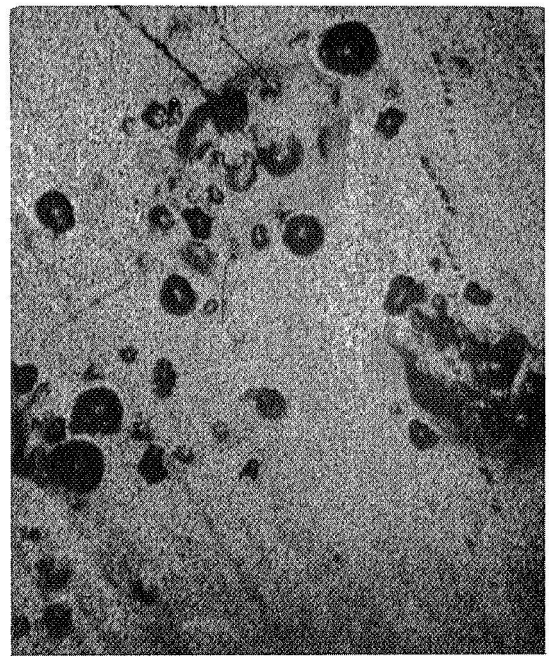
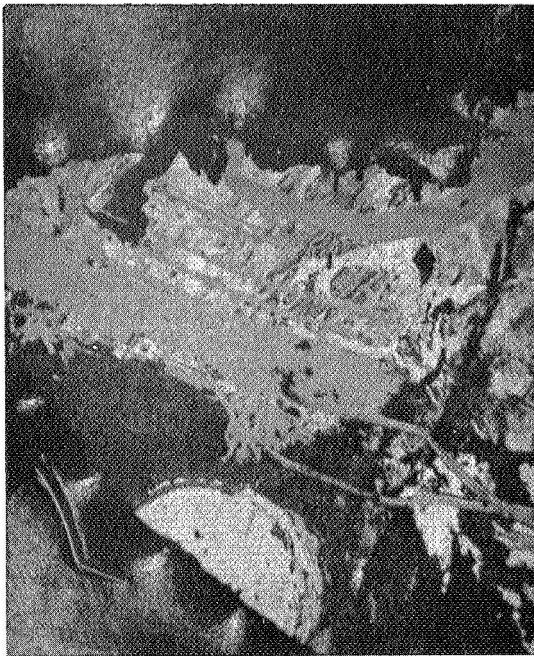
150°C CONTACT ELECTRON MICROSCOPE
PHOTO NEGATIVE REPLICA

CA19783

Figure 5. 150°C Contacts Electron Microscope Photos



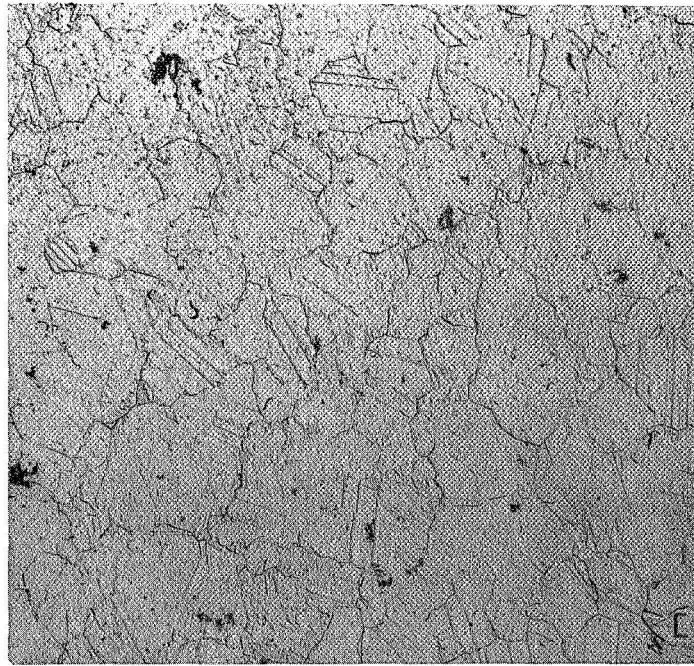
100°C N-CONTACT BLISTERS (60X)



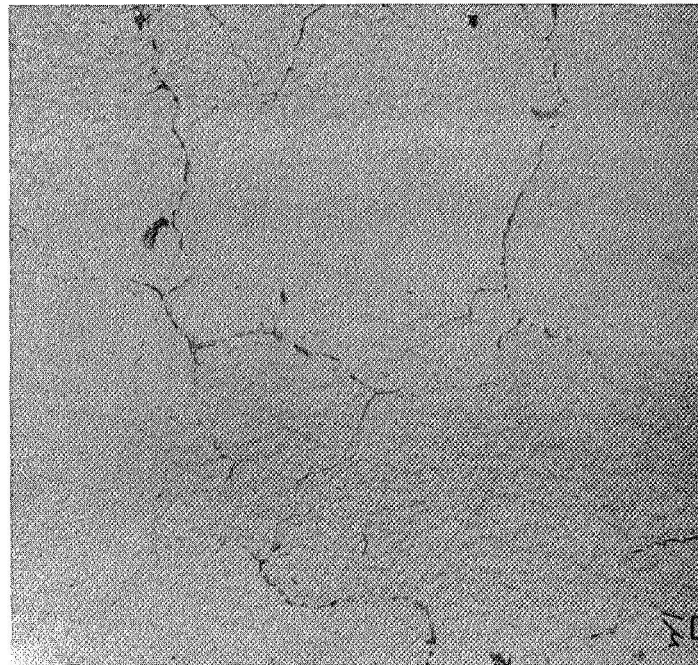
100°C P-CONTACT BLISTERS (60X)

CA19784

Figure 6. 100°C Contacts After Environmental Testing



100°C CONTACT ELECTRON MICROSCOPE
PHOTO POSITIVE REPLICA



100°C CONTACT ELECTRON MICROSCOPE
PHOTO NEGATIVE REPLICA

CA19785

Figure 7. 100°C Contacts Electron Microscope Photos

Table II. 150°C Substrate Electrical Data

Cell No.	$I_{SC}(mA)$	$I_{SC}(mA)$	Δ	$V_{OC}(mV)$	$V_{OC}(mV)$	Δ	I at 430 mV (mA)	I at 430 mV (mA)	Δ
	Initial	Post	(mA)	Initial	Post	(mV)	Initial	Post	(mA)
Control Cell	149.0	150.0	+1.0	566	566	0	142.3	143.0	+0.7
C-1	147.3	149.2	+2.1	553	553	0	140.1	140.1	0
C-2	155.0	156.0	+1.0	555	555	0	146.0	146.0	0
C-3	150.0	151.0	+1.0	553	553	0	140.0	135.0	-5.0
C-4	151.0	152.8	+1.8	556	556	0	144.2	144.2	0
C-5	145.0	146.0	+1.0	553	553	0	136.4	135.8	-0.6
C-6	151.0	162.0	+11.0	556	575	+19	142.0	96.0	-46.0
C-7	153.8	154.0	+0.2	552	552	0	141.8	134.0	-7.8
C-8	147.3	148.6	1.3	555	558	+3	138.8	137.7	-1.1
C-9	148.8	150.0	+1.2	554	554	0	138.0	128.0	-10.0
C-10	151.0	151.5	+0.5	557	557	0	144.0	144.0	0
Average	150.0	152.1	+2.1	554.4	556.6	+2.2	141.13	134.08	-7.05

d. 50°C Substrate Temperature—Group A

Electron microscopy of these cells shows a contact grain size and structure very similar to Group B, however it was noted that the cracks in the grain boundary area of Group A are much larger and more exaggerated. Electron microscopy photos of this group are presented in Figure 8. In Table IV a significantly higher power loss is seen in this group when compared to the other groups. It is suspected that this power loss is the effect seen when the titanium layer is extensively reacted to form an insulating film between the silver and silicon. Blisters and peeling were predominant in this group as shown in Figure 9. Nine out of ten cells in this group had an electrical output loss greater than 4.5 percent at the maximum power point.

e. 0°C Substrate Temperature—Group E

Electron microscope photos of this group show a contact grain structure very different from any of the other groups. As can be seen in Figure 10, there is a definite lack of large cracked grain boundary areas. Electrical data presented in Table V indicate that this group of cells does exhibit more degradation resistance than any group reported. None of the sample cells in Group E had a loss in electrical output greater than 4.1 percent after exposure in the temperature and humidity chamber. Blisters still occurred on this group but were generally smaller and more isolated. One cell from this experiment would not survive the solar panel soldering processes after environmental exposure. Twenty cells from this experiment have been shipped to NASA GSFC for evaluation.

Table III. 100°C Substrate Electrical Data

Cell No.	I_{SC} (mA)	I_{SC} (mA)	Δ	V_{OC} (mV)	V_{OC} (mV)	Δ	I at 430 mV (mA)	I at 430 mV (mA)	Δ
	Initial	Post	(mA)	Initial	Post	(mV)	Initial	Post	(mA)
Control Cell	148.0	148.0	0	556	556	0	138.3	138.0	-0.3
B-1	147.2	148.0	+0.8	553	553	0	139.8	133.2	-6.6
B-2	149.0	149.5	+0.5	548	548	0	138.1	136.1	-2.0
B-3	146.0	146.0	0	560	560	0	139.5	139.4	-0.1
B-4	149.2	149.8	+0.6	558	558	0	142.2	142.3	+0.1
B-5	145.5	145.6	+0.1	553	553	0	138.2	138.2	0
B-6	137.9	137.8	-0.1	535	535	0	124.0	123.8	-0.2
B-7	144.0	144.0	0	555	555	0	136.0	137.0	+1.0
B-8	145.8	49.2	-96.6	553	540	-13	135.8	2.0	-133.8
B-9	145.2	145.8	+0.6	558	558	0	138.2	136.0	-2.2
B-10	147.8	147.2	-0.6	553	550	-3	140.2	139.0	-1.2
Average	145.76	136.29	-9.47	552.6	551.0	-1.6	137.2	122.7	-14.5

2. Sintering Gases

A group of silicon solar cells having blistered Ti-Ag contacts were subjected to a mass-spectrometer residual gas analysis. Hydrogen was found to be concentrated in the Ti-Ag contact blisters. This analysis was performed by evacuating the analysis chamber and then crushing the blistered contact samples. It was then felt that hydrogen from the forming gas (10% H_2 + 90% N_2) could possibly diffuse into the contact during the sintering operation and contribute to the appearance of blisters after exposure to temperature and humidity. In order to evaluate a possible contributing factor to the temperature-humidity resistance of Ti-Ag contacts on silicon solar cells, TI processed four groups of cells on which the ambient gas during the contact sintering operation was changed. Separate groups of cells were sintered using ambients of forming gas, hydrogen, nitrogen and helium. Environmental exposure of these cells resulted in equal blistering of each of the four groups as shown in Figure 11. The presence or absence of hydrogen during the sintering process apparently does not contribute to the temperature-humidity resistance of Ti-Ag contacts on silicon solar cells. It is now felt that the concentrated hydrogen found in the blistered areas is a result of the chemical reaction on the contact where moisture acts as a catalyst.

3. Contact Silver Thickness

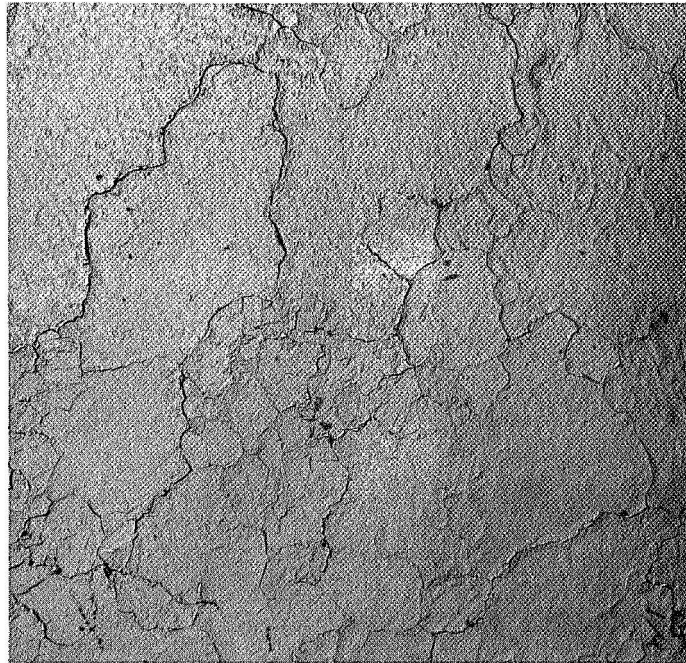
Silicon solar cells with silver contact thicknesses of 3, 5, 7, and 10 microns have been fabricated and are now in the temperature and humidity environmental chamber. These results will be reported in the next quarterly report.

Table IV. 50°C Substrate Electrical Data

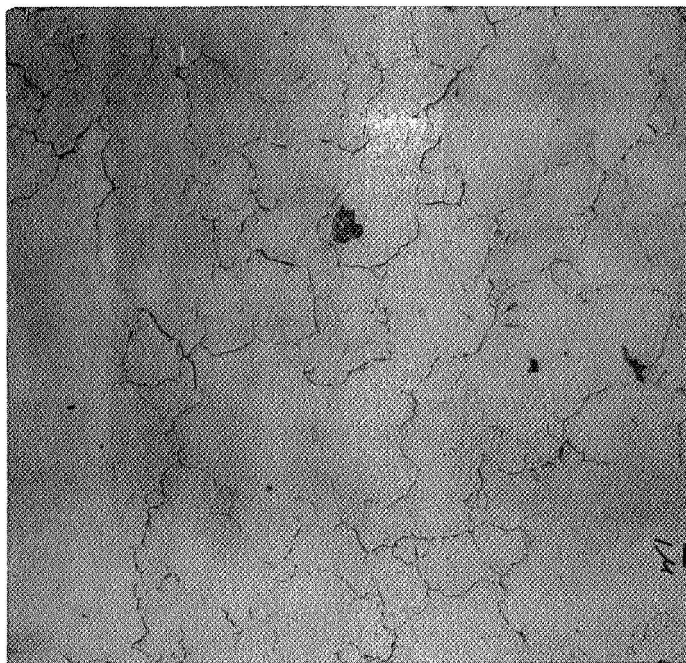
Cell No.	I_{SC} (mA)	I_{SC} (mA)	Δ	V_{OC} (mV)	V_{OC} (mV)	Δ	I at 430 mV (mA)	I at 430 mV (mA)	Δ
	Initial	Post	(mA)	Initial	Post	(mV)	Initial	Post	(mA)
Control Cell	152.0	152.2	+0.2	560	560	0	140.3	140.2	-0.1
A-1	149.2	149.8	+0.6	565	565	0	140.6	114.0	-26.6
A-2	142.9	142.2	-0.7	567	567	0	136.1	120.0	-16.1
A-3	150.1	149.0	-1.1	563	555	-8	144.0	124.8	-19.2
A-4	150.8	143.2	-7.6	561	556	-5	141.0	52.0	-89.0
A-5	146.0	112.5	-33.5	560	560	0	138.0	7.0	-131.0
A-6	145.9	144.0	-1.9	565	560	-5	139.5	135.9	-3.6
A-7	150.3	124.8	-25.5	568	560	-8	144.8	6.8	-138.0
A-8	152.0	151.2	-0.8	563	556	-7	146.0	137.8	-8.2
A-9	145.8	145.6	-0.2	560	560	0	139.0	131.9	-7.1
A-10	144.0	143.0	-1.0	550	548	-2	135.0	118.0	-17.0
Average	147.7	140.53	-7.17	562.2	558.7	-3.5	140.4	94.82	-45.58

Table V. 0°C Substrate Electrical Data

Cell No.	I_{SC} (mA)	I_{SC} (mA)	Δ	V_{OC} (mV)	V_{OC} (mV)	Δ	I at 430 mV (mA)	I at 430 mV (mA)	Δ
	Initial	Post	(mA)	Initial	Post	(mV)	Initial	Post	(mA)
Control Cell	147.7	148.5	+0.8	558	558	0	141.7	141.6	-0.1
E-1	146.6	147.3	+0.7	562	553	-9	140.8	139.8	-1.0
E-2	146.8	145.7	-1.1	556	552	-4	138.0	135.2	-2.8
E-3	145.8	145.7	-0.1	559	559	0	139.1	138.0	-1.1
E-4	145.0	144.0	-1.0	558	554	-4	137.7	136.7	-1.0
E-5	145.0	144.1	-0.9	553	550	-3	135.4	135.0	-0.4
E-6	146.5	146.4	-0.1	558	558	0	136.0	135.8	-0.2
E-7	146.3	146.2	-0.1	548	548	0	138.0	137.4	-0.6
E-8	146.2	146.2	0	558	555	-3	139.0	138.5	-0.5
E-9	148.0	146.0	-2.0	549	548	-1	137.4	132.0	-5.4
E-10	145.0	144.8	-0.2	558	557	-1	139.0	137.6	-1.4
Average	146.12	145.64	-0.48	555.9	553.4	-2.5	138.04	136.6	-1.44



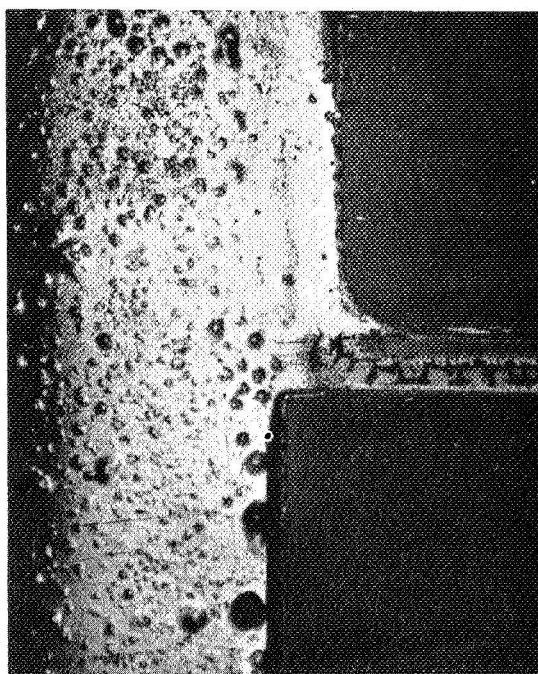
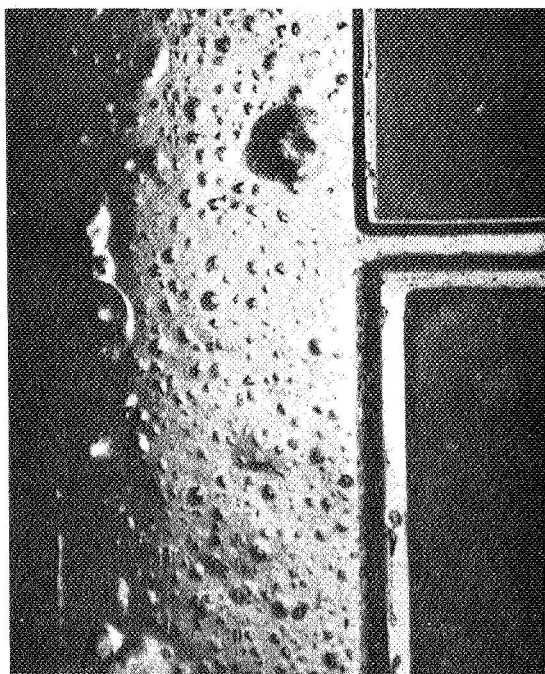
50°C CONTACT ELECTRON MICROSCOPE
PHOTO POSITIVE REPLICA



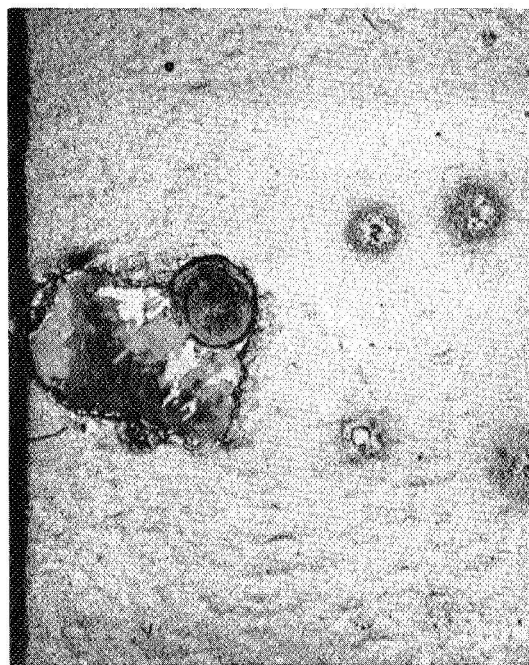
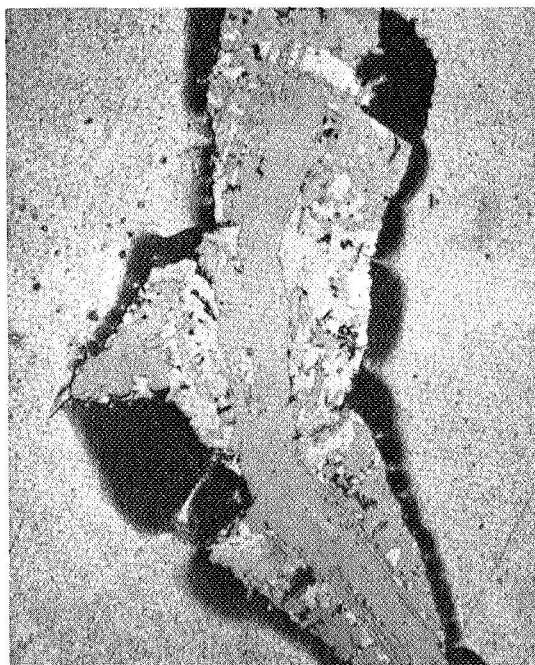
50°C CONTACT ELECTRON MICROSCOPE
PHOTO NEGATIVE REPLICA

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Figure 8. 50°C Contacts Electron Microscope Photos



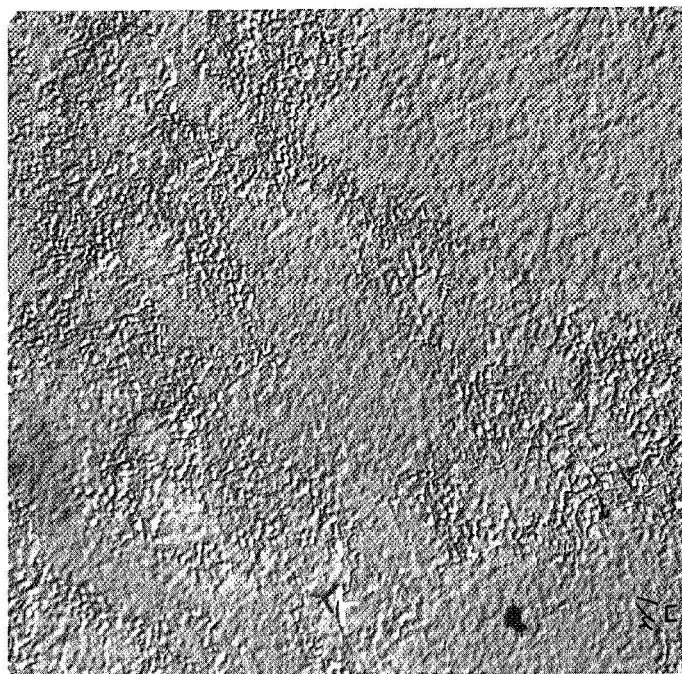
50°C N-CONTACT BLISTERS (60X)



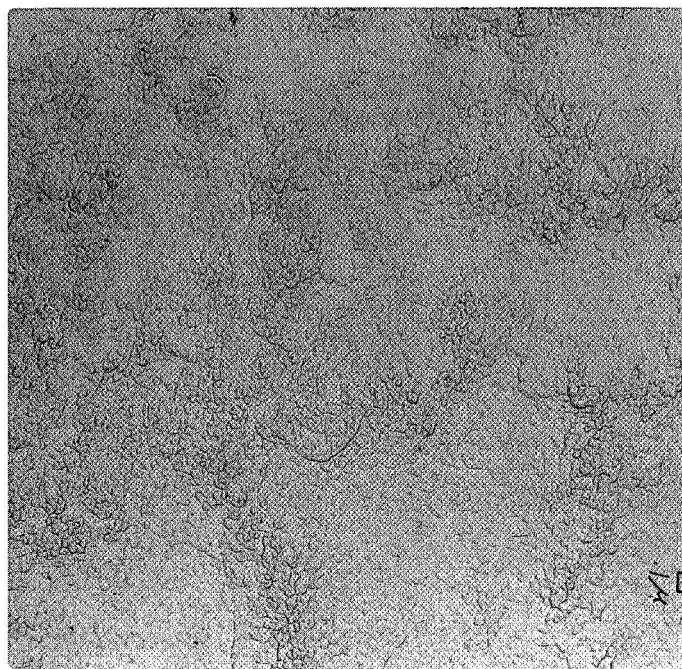
50°C P-CONTACT BLISTERS (60X)

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Figure 9. 50°C Contacts After Environmental Testing



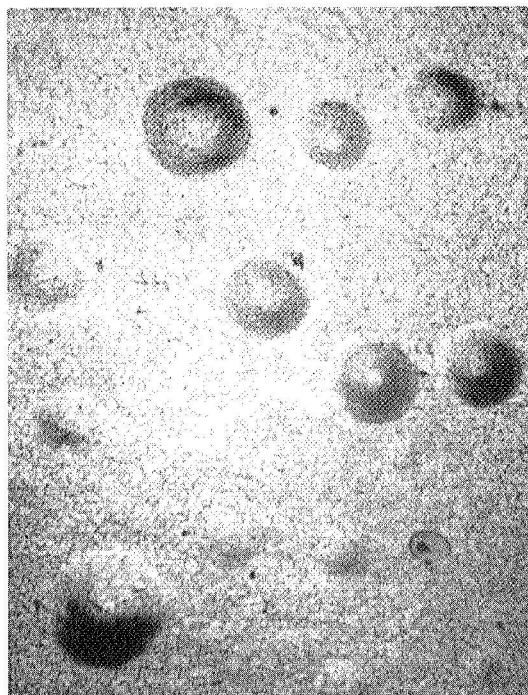
0°C CONTACT ELECTRON MICROSCOPE
PHOTO POSITIVE REPLICA



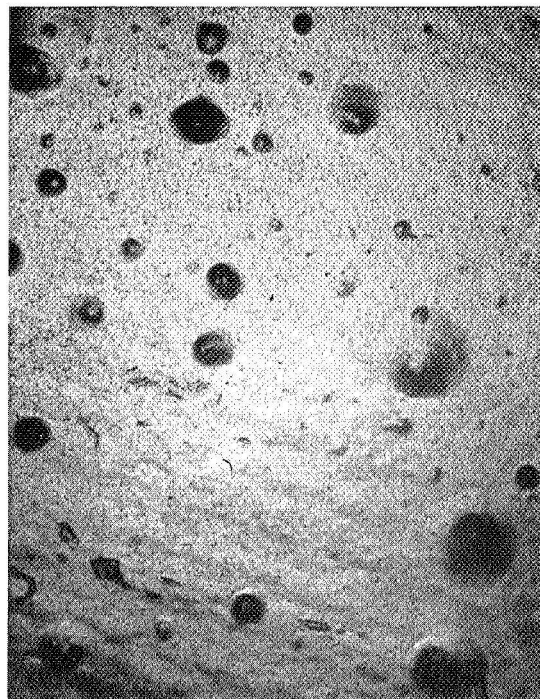
0°C CONTACT ELECTRON MICROSCOPE
PHOTO NEGATIVE REPLICA

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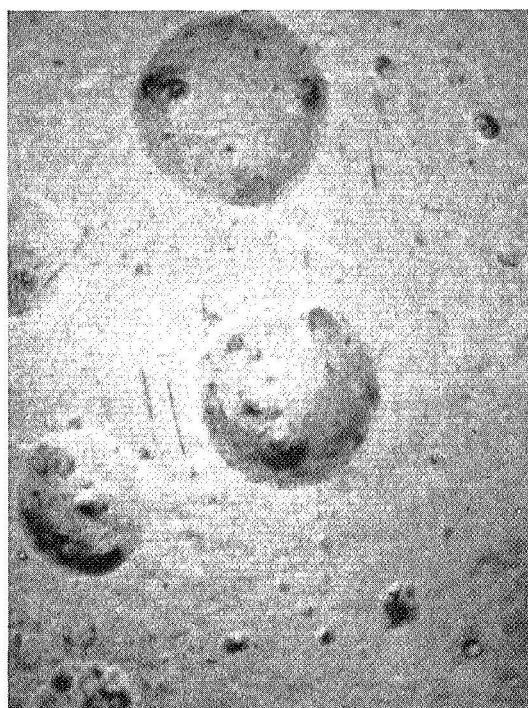
Figure 10. 0°C Contacts Electron Microscope Photos



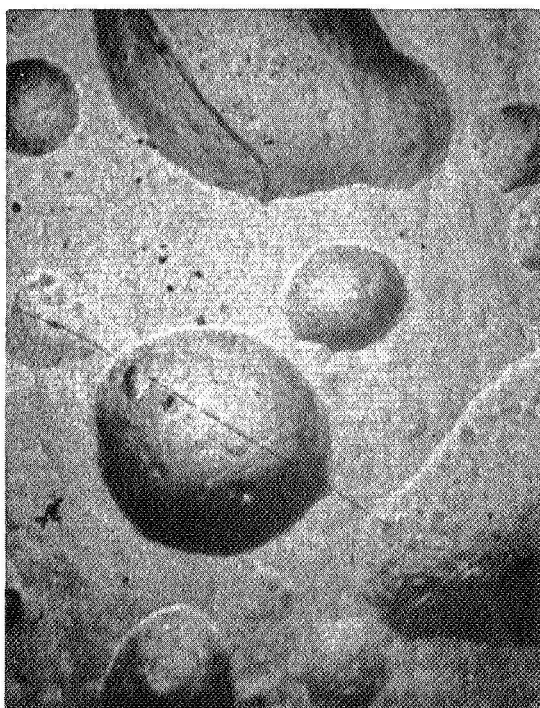
CONTACTS SINTERED IN FORMING GAS
(10% H_2 + 90 N_2) (60X)



CONTACTS SINTERED IN PURE
HYDROGEN (60X)



CONTACTS SINTERED IN HELIUM (60X)



CONTACTS SINTERED IN NITROGEN (60X)

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Figure 11. Contacts Sintered in Different Ambient Gases

SECTION III

NEW TECHNOLOGY

New technology reported this period includes the evaporation of Ti-Ag contacts onto silicon solar cells while maintaining a substrate temperature of 0°C. This technique resulted in a silver grain structure considerably different than was previously experienced. This contact shows some evidence of improvement on the Ti-Ag contact temperature and humidity resistance. Solar cells with this type of contact evaporation have been submitted to NASA GSFC for final evaluation.

SECTION IV

PROGRAM FOR NEXT REPORTING PERIOD

The next report on this study program will be the final report, and will include work performed during the next quarter which includes December 1968, January 1969, and February 1969. During this period, it is planned to complete the evaluation of the silver thickness experiment. Contact evaporation rates will be studied as well as vacuum sintering and contacts evaporated in a turbo-molecular vacuum system. In addition to the above, TI plans to study the possibility of including a third metal into the Ti-Ag contact system, which would alter the electrochemical potential between the Ti and the Ag. TI plans to perform this experiment under TI in-house funding.

SECTION V

CONCLUSIONS AND RECOMMENDATIONS

1. Evaluations performed during this reporting period indicate that evaporation substrate temperatures contribute to the optimization of the temperature-humidity resistance of the Ti-Ag contacts on silicon solar cells by influencing the grain size and structure of the evaporated metal. Experimental results show that contacts deposited at reduced substrate temperatures exhibit smaller grain size and a higher degree of temperature-humidity resistance.
2. Sintering ambient gases do not have an effect on the temperature-humidity resistance of the Ti-Ag contacts on silicon solar cells.

While it appears that the Ti-Ag contact system may indeed be improved, it is felt that work should also begin with the objective of finding a new contact system which will remain stable under storage conditions on earth or operating conditions in space environments.